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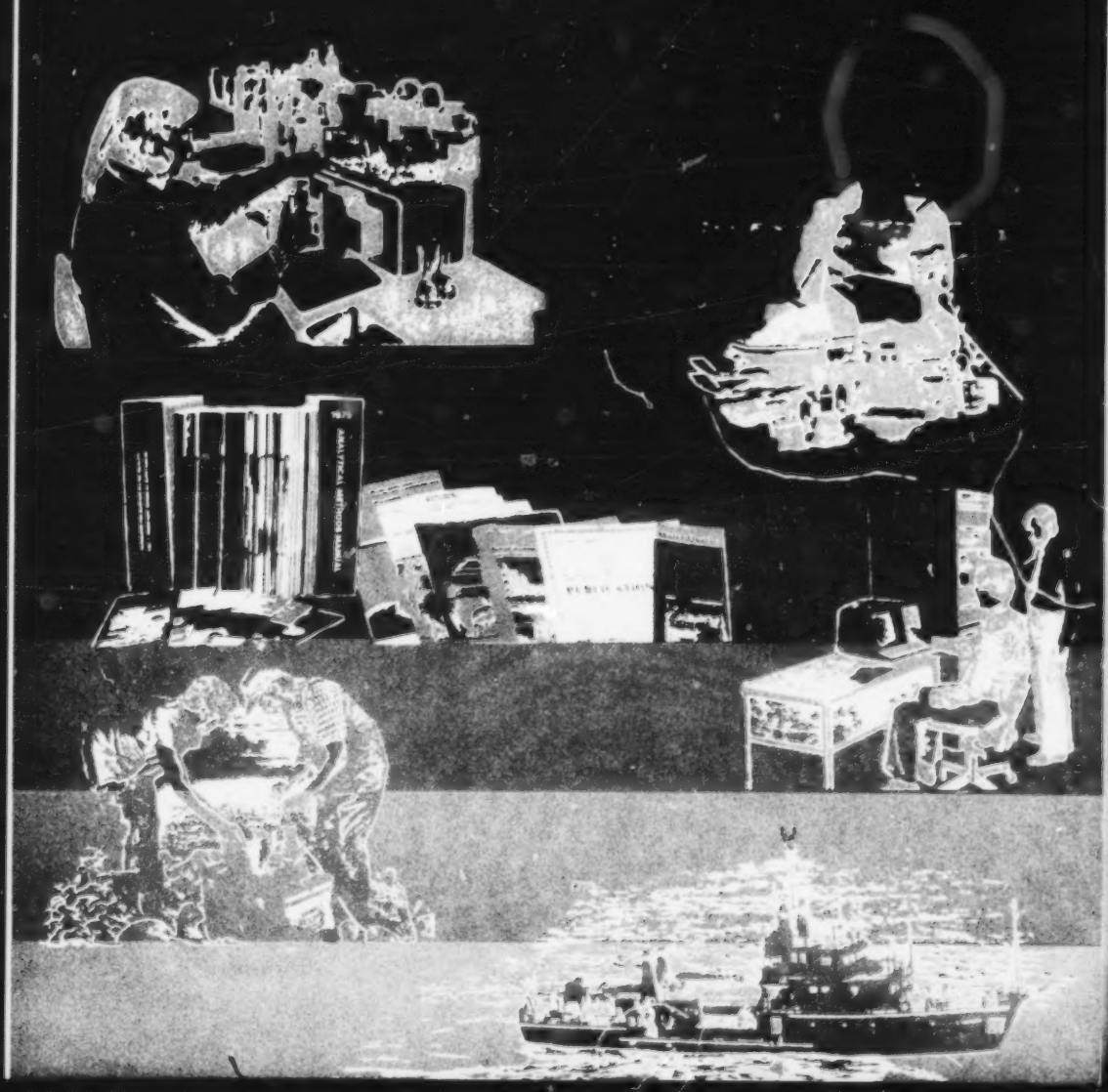
Canada

Polynuclear Aromatic Hydrocarbons in Bottom Sediment Samples of Rivers, Lakes and Harbours



Polynuclear Aromatic Hydrocarbons in Bottom Sediment Samples of Rivers, Lakes and Harbours

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ABSTRACT

The Water Quality Branch, Inland Waters Directorate, carried out a national survey to obtain a broad indication of typical ranges of polycyclic aromatic hydrocarbons (PAHs) in the aquatic environment. Thirty sites were sampled and the concentrations of fluoranthene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (g,h,i) perylene, benzo (a) pyrene and indeno (1,2,3-cd) pyrene were determined.

RESUME

La Direction de la qualité des eaux, Direction générale des eaux intérieures, a effectué une étude à l'échelle nationale afin d'obtenir une indication générale des écarts types de concentration pour les hydrocarbures aromatiques polycycliques (HAP) dans le milieu aquatique. Au total, des échantillons ont été prélevés en trente endroits pour déterminer la concentration du fluoranthène, du benzo (b) fluoranthène, du benzo (k) fluoranthène, du benzo (g,h,i) périylène, du benzo (a) pyrène et de l'indéno (1,2,3-cd) pyrène.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are widely distributed in the environment. Their carcinogenic properties make their presence in the aquatic environment a cause for concern. To obtain a broad indication of typical ranges of PAHs in the Canadian environment the Water Quality Branch (WQB), Inland Waters Directorate, carried out a national survey for PAHs in the bottom sediment of "pristine" as well as potentially contaminated aquatic environments. Bottom sediments were chosen for analysis because PAHs accumulate there. A related purpose of the project was to identify areas that may require additional investigation. Thirty sites across Canada (Fig. 1) and Appendix A were sampled and the concentrations of fluoranthene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (g,h,i) perylene, benzo (a) pyrene and indeno (1,2,3-cd) pyrene were determined.

METHODOLOGY

Sample Collection

The sediment samples were collected across Canada by WQB personnel using predetermined sampling methods (WQB, 1983), during the fall of 1981. All samples were frozen in glass containers and remained frozen during storage until they were thawed for analysis.

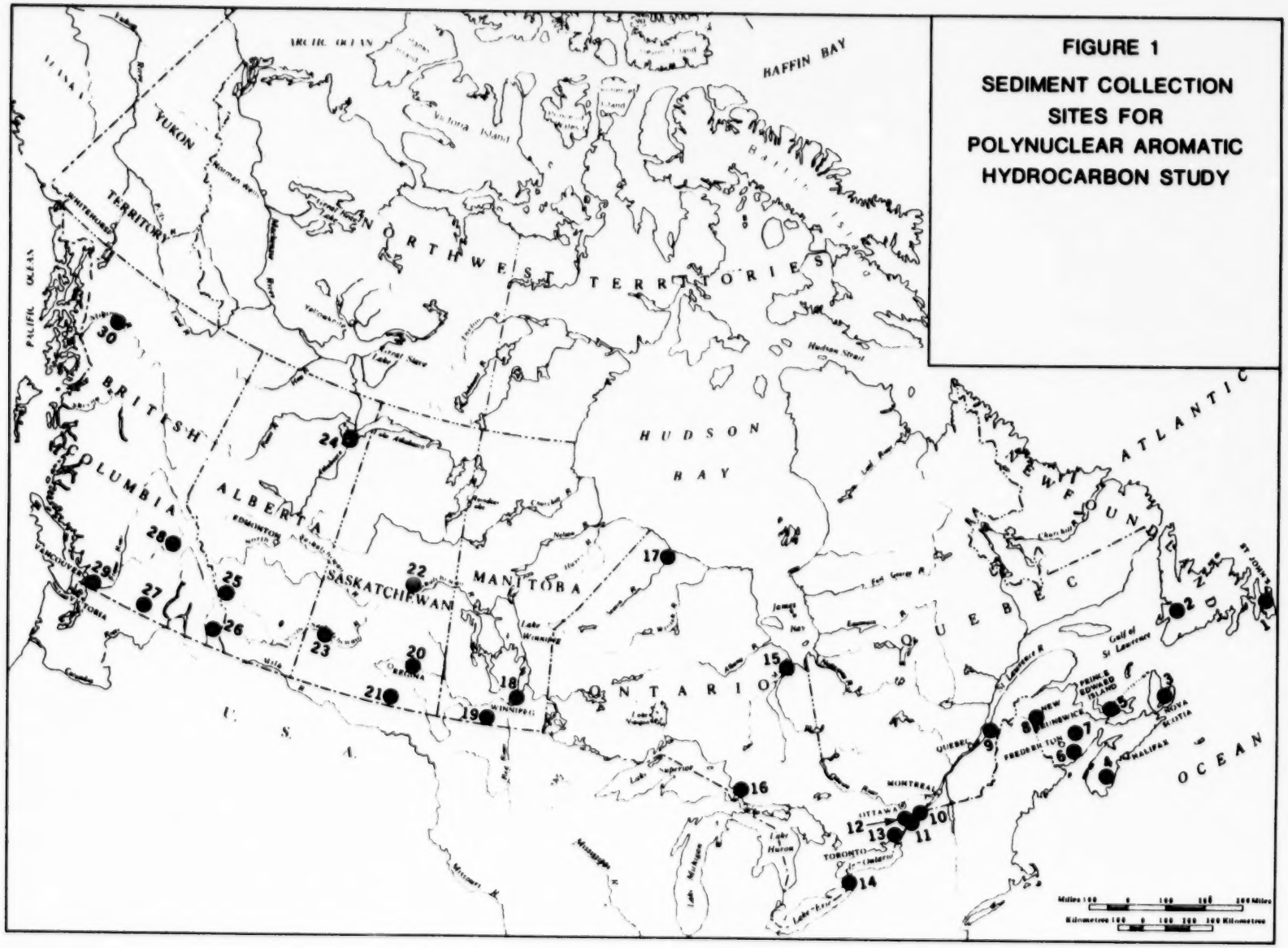
FIGURE 1
SEDIMENT COLLECTION
SITES FOR
POLYNUCLEAR AROMATIC
HYDROCARBON STUDY
ARCTIC OCEAN
BAFFIN BAY
YUKON
TERRITORY
NORTHWEST TERRITORIES
HUDSON
BAY
BRITISH
COLUMBIA
ALBERTA
SASKATCHEWAN
MANITOBA
ONTARIO
QUEBEC
NEWFOUNDLAND
ATLANTIC
OCEAN
U. S. A.
PRINCE EDWARD ISLAND
NOVA SCOTIA
NEW BRUNSWICK
HALIFAX
MONTREAL
OTTAWA
TORONTO
WINNIPEG
EDMONTON
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Distribution of the 30 sampling sites by province and by type of water is shown in Table 1. The detailed list of sampling locations is given in Appendix A. One site in Ontario was sampled in three different places along one transect of the river. Similarly, three sites in British Columbia were sampled at two different points each. This type of sampling gives an indication of the variability of concentration values at a given location. Thirty-five different points were sampled in triplicate, for a total of 105 samples.

Analytical Procedure

Six PAHs recommended for monitoring purposes by the World Health Organization were selected for analysis. These compounds are benzo (b) fluoranthene, benzo (a) pyrene and indeno (1,2,3-cd) pyrene, known to be carcinogenic to animals and probably to man; and benzo (k) fluoranthene, benzo (g,h,i) perylene and fluoranthene considered to be non-carcinogenic. The laboratory analyses were done under contract by Cantest Ltd. (Vancouver, B.C.). The samples were identified only by a number; the location from which they were collected and the sampling date were not provided to the contractor.

The analytical procedure used was that of Afghan and Wilkinson (1981). Using a Polytron homogenizer sediments are nomogenized and then extracted with 20 mL of acetone. The contents are then centrifuged using a clinical centrifuge, and the acetone supernatant is decanted into

Table 1. Distribution of Sampling Sites by Province and Type of Water

Province	No. of sites per water type			
	Rivers, streams	Lakes, reservoirs	Harbours, bays	Total
Newfoundland			2	2
Nova Scotia			2	2
Prince Edward Island			1	1
New Brunswick	1	1	1	3
Quebec		3		3
Ontario	5	1		6
Manitoba	1	1		2
Saskatchewan		4		4
Alberta	1	1		2
British Columbia	5			5
Total	13	11	6	30

a 2-L separatory funnel. The acetone extraction is repeated and the supernatant transferred into the same separatory funnel. Millipore water (1.5 L) is added to the acetone extracts and the mixture is extracted with hexane. The resultant extract is concentrated and cleaned up by gel permeation and alumina column chromatography. The cleaned and concentrated extract is analyzed for PAHs by isocratic reverse phase high pressure liquid chromatography (HPLC) using a mobile phase of 82% acetonitrile in water. The chromatographed extract is then sequentially fed into a flow-through ultraviolet (U.V.) absorption detector at 254 nm and 280 nm, and a fluorescence detector with excitation at 280 nm and emission at 389 nm. Quantitation is done by comparing the peak height or integrated peak area of sample peaks with peaks of standards obtained under the conditions described above.

The reverse phase column (Dupont 5 μm Zorbac ODS) completely separates fluoranthene, benzo(a) pyrene, indeno (1,2,3-cd) pyrene and benzo (g,h,i) perylene. The other two compounds, benzo (b) fluoranthene and benzo (k) fluoranthene, elute together and are determined quantitatively on specific detectors.

Positive identification of the various PAHs was confirmed by adding an internal standard to the final extracts and then calculating the relative retention times for all PAHs. The choice of internal standard depended on the nature of the chromatogram obtained for a given sample and the number of PAHs present in the sample. The internal

standard PAH was chosen so that its peak occurred in an area of the chromatogram which was relatively clean, and the sample itself did not contain significant amounts of the standard compound.

Additional confirmation was obtained by comparing the retention times, using multicolumn techniques. This was done by running the sample using different normal and/or reverse phase liquid chromatographic columns with different solvents and different compositions for the mobile phase (isocratic as well as gradient elution). Confirmation was also made by absorption and fluorescence response ratios and by monitoring the absorption or fluorescence with specific detectors. Further confirmation of individual PAHs was obtained by collecting various fractions containing co-eluting peaks and carrying out a full spectral identification, using absorptiometry or molecular fluorescence. Final confirmation of PAHs was achieved in some samples using a GC/MS system with suitable data handling capabilities.

Quality Control

To ensure and determine the quality of the laboratory results, five reference sediment samples were submitted for analysis. Triplicate analyses were carried out on these samples. The relative standard deviations (RSD) had a range of approximately 15% to 75%, with a few values at less than 15%. The RSD values did not show any specific pattern with respect to the type of compound or the concentration range.

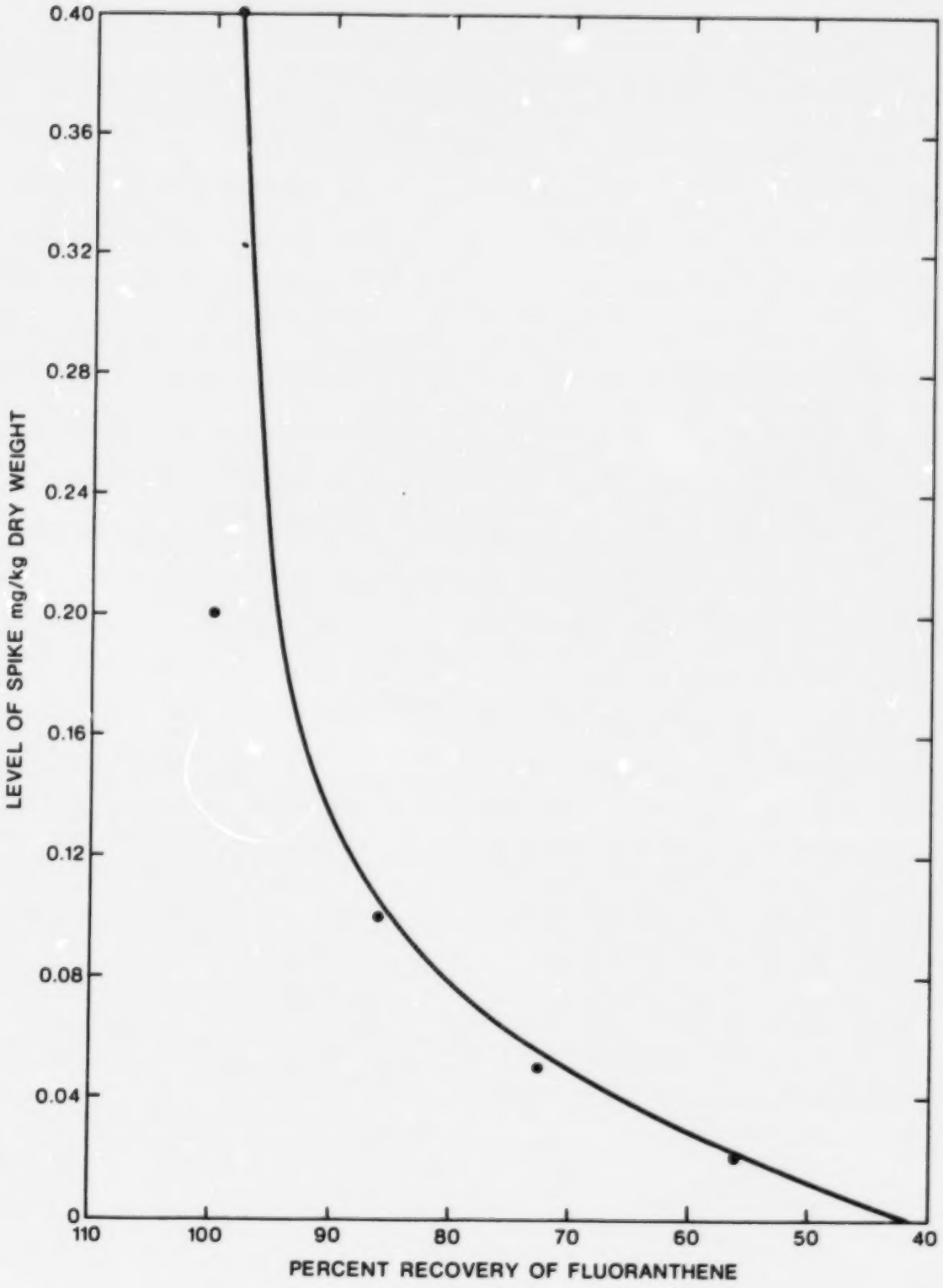
In addition, a number of "blind" reference samples interspersed with the project samples were submitted, identified only by a sample number. Based on the mean and standard deviation obtained for the initial five reference sediment samples, all determinations of the blind reference samples had to agree within three standard deviations of the mean value. When this requirement was not met, WQB decided whether or not all or part of a batch of analyses were to be reanalyzed.

To correct for recovery losses, correction factors were calculated by spiking 12 samples with the six compounds of interest with amounts of 0.01-4.0 mg/kg (dry weight basis) and then analyzing the samples following the normal analytical procedure. A recovery curve was generated for each of the six compounds. The recovery curve for fluoranthene is shown as an example in Figure 2. The curve shows the increase in recovery from a low of 56% at a concentration of 0.01 mg/kg to 98% at 0.40 mg/kg. A correction factor (CF) for a range of concentrations was then calculated from the following expression:

$$CF = \frac{100\%}{\%\ \text{recovery}}$$

For example, for range 0.08-0.12 mg/kg the mean recovery was 84% and CF = 1.19. The correction factors ranged from 1.0 to 2.94. As expected, the low CFs corresponded to high concentrations and the high CFs to low concentrations. The recovery of all six compounds was greater than 95% at a spiking level of 0.32 mg/kg or greater. At spiking levels below 0.32 mg/kg, the recoveries decreased along smooth curves to a low value

FIGURE 2. RECOVERY CURVE FOR FLUORANTHENE



of 40% for benzo (g,h,i) perylene and indeno (1,2,3-cd) pyrene at a spike level of 0.02 mg/kg. The complete list of correction factors is given in Appendix D.

Several factors, such as the amount of extractants in different samples and the sorption of PAHs onto suspended particles, can contribute to the different recoveries. In this study no attempt has been made to explain these different recoveries. Future studies should address this topic, perhaps as part of quality assurance.

PROPERTIES OF POLYNUCLEAR AROMATIC HYDROCARBONS

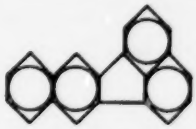
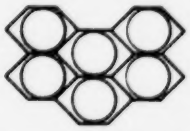
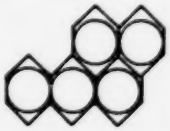
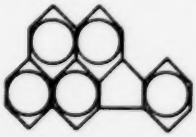
Polynuclear (polycyclic) aromatic hydrocarbons (PAHs) are fused (condensed) ring aromatic compounds with two or more carbon atoms per ring shared between two or more rings. Polynuclear aromatic hydrocarbons include hundreds of compounds with widely varying physical, chemical and biological properties. For the most part they are characterized as being high melting, high boiling point solids with low vapour pressures at ambient temperature and atmospheric pressure. They are practically insoluble in water. It was estimated that water solubilities of most PAHs with more than three rings in their molecular structure are of the order of 10^{-10} moles/L or less (Radding et al., 1976). Polynuclear aromatic hydrocarbons exhibit much higher solubilities in aromatic and other organic solvents. The octanol-water partition coefficients are of the order of 10^{4}-10^{6} (Radding et al., 1976). This indicates that

significant bioconcentration of PAHs might occur in fatty tissues of living organisms and might also bioaccumulate along the food chain. Equally significant from the point of view of environmental fate and biological activity is the fact that solubilization of PAHs in water occurs to an appreciable extent by the addition of various surface-active agents, naturally occurring humic acid derivatives, proteins, purines and nucleic acids.

Table 2 provides information regarding structure, molecular formula, molecular weight and other names for the compounds analyzed in this project. Table 3 outlines their physical properties.

Chemically, PAHs are reactive compounds which undergo all the characteristic reactions of aromatic systems, namely electrophilic substitutions, 1,2-additions, 1,4-additions, eliminations and radical reactions. The type of reaction depends on the nature of the particular PAH compound and the reagent. Polynuclear aromatic hydrocarbons are generally more reactive than simple benzene derivatives, owing to the possibility of stabilization of the reactive transition-state species by extensive delocalization of electrons. The facile removal of one electron from polycyclic systems to form a cation leads to the formation of oxidized products such as endoperoxides, diols, quinones and dimers (Clar, 1964).

Table 2. Chemical Characteristics of Selected PAHs

Compound	Structure	Molecular formula	Molecular weight	Other names
Fluoranthene CAS:206-44-0* TSL: LL40250**		$C_{16}H_{10}$	202.24	Benzo [j,k] fluorene Idrye
Benzo (b) Fluoranthene CAS: 205-99-2 TSL: CU14000		$C_{20}H_{12}$	252.32	Benz(e)acephenanthrylene 2,3-Benzofluoranthene 3,4-Benzofluoranthene Benzo(e)fluoranthene
Benzo (k) Fluoranthene CAS: 207-08-9 TSL: DF63500		$C_{20}H_{12}$	252.32	11,12-Benzofluoranthene
Benzo(g,h,i) Perylene CAS: 191-24-2 TSL: DI62005		$C_{22}H_{12}$	276.34	1,12-Benzoperylene
Benzo (a) Pyrene CAS: 50-32-8 TSL: DJ36750		$C_{20}H_{12}$	252.32	1,2-Benzopyrene 3,4-Benzopyrene BaP
Indeno (1,2,3-cd) Pyrene CAS: 193-39-5 TSL: NK93000		$C_{22}H_{12}$	276.34	2,3-Phenylenepyrene 2,3-o-Phenylenepyrene IP

* Chemical Abstracts Service No.

** Registry of Toxic Effects of Chemical Subs ances, 1976 Edition. National Institute for Occupational Safety and Health, Cincinnati, Ohio (Also know as RTECS No.)

Ref. 1 MOE, 1979. Polynuclear Aromatic Hydrocarbons - A Background Report Including Available Ontario Data - ARB-TDA-Report No. 58-79, September 1979.

Ref. 2 EPA, 1979. Water-Related Environmental Fate of 129 Priority Pollutants. Vol. II. EPA-440/4-79-0296, Washington, D.C.

Table 3. Physical Properties of Selected PAHs

Compound	Solubility	Octanol/ water part. coeff.	Melting point (°C)	Boiling point (°C @ 1 ATM)	Density	Vapour pressure @ 25°C (TORR)	Equilibrium vapour conc.@ 25°C (ng/m^3)
Fluoranthene	Water 0.26 mg/L soluble in most organic solvents	5.33	110-111	393	1.252	10^{-6}-10^{-4}	
Benzo (b) Fluoranthene	Almost insoluble in water, slightly soluble in alcohol	6.57	167-168			10^{-11}-10^{-6}	
Benzo (k) Fluoranthene	Almost insoluble in water, soluble in alcohol, benzene acetic acid.	6.84	216-217	480		9.59×10^{-11}	13
Benzo (g,h,i) Perylene	Water: 0.000 26 mg/L slightly soluble in benzene, ethanol.	7.23	222			1.01×10^{-10}	1.5
Benzo (a) Pyrene	Water: 0.0038 mg/L water, slightly soluble in ethanol, methanol. Soluble in benzene, toluene, xylene.	6.04	176.5-177.5 (also 179)	475	1.351	5.49×10^{-9}	75
Indeno (1,2,3-cd) Pyrene	Almost insoluble in water, soluble in aromatic solvents, cyclohexane.	7.66	162.5-164				

Ref. 1. Polynuclear Aromatic Hydrocarbons - A Background Report Including Available Ontario Data - ARB-TDA-Report No. 58-79 September 1979.
Ref. 2. EPA 1979. Water Related Environmental Fate of 129 Priority Pollutants. Vol. II EPA-440/4-79-029b, Washington, D.C.

SOURCES, PATHWAYS AND FATE OF PAHs IN THE ENVIRONMENT

Polycyclic aromatic hydrocarbons are widely distributed in the environment. They have been found in animal and plant tissues, sediments, soils, air, industrial effluents, surface and drinking water (EPA, 1979). The presence of PAHs in the environment is the result of both anthropogenic and natural processes. Polynuclear aromatic hydrocarbons are produced as a result of incomplete combustion of almost all organic matter, including coal, oil, wood, natural gas, various animal and vegetal lipids, carbohydrates, proteins and amino acids.

Forest fires and volcanic eruptions are natural sources that have contributed to man's exposure to PAHs since prehistoric times (MOE, 1979). Other natural sources of PAHs may possibly include biosynthesis by lower organisms and low-temperature natural processes involving decaying organic matter. Consequently, PAHs probably have been present in the environment for many thousands of years before their levels dramatically increased with human industrial activity.

The anthropogenic sources of PAHs can be of an industrial or a non-industrial nature. Non-industrial sources include cigarette smoking (the single most significant source of direct personal exposure to carcinogenic PAHs), homecooking, frying, smoking, roasting and charbroiling of foods, agricultural burning, home heating, as well as leisure-type activities involving the use of internal combustion engines such as outboard motors and gasoline-powered lawn

mowers (HWC, 1979; MOE, 1979). Industrial sources are related to such processes as coke production for the iron and steel industry, catalytic cracking in the petroleum industry and the production of carbon black, coal tar pitch, asphalt, hot road mix processes, general chemical processes, as well as heating and power generation. Other sources include controlled refuse incineration, open burning and internal combustion engines for various means of transportation. While transportation sources account for only about 1% of the emitted PAHs on a national inventory basis, transportation-generated PAHs may approach 50% of the urban resident exposures (EPA, 1976).

The mechanism of PAH formation during combustion is complex and depends on a number of factors including temperature, nature of the combustible material, time and the availability of an oxidizing or reducing atmosphere. Aliphatic carbon to carbon bonds and carbon to hydrogen bonds break down relatively readily at pyrolysis temperatures (500°C-800°C), yielding molecular fragments of free-radical nature which then undergo recombinations. At the temperatures of pyrolysis and in chemically reducing atmospheres, "prevailing at the centre of flames," aromatic ring systems are the most stable of the various molecular species present and their relative stability leads to the gradual accumulation of condensed aromatic structures of increasing complexity as the pyrolysis and pyrosynthesis progresses during the combustion process. The amount of PAHs formed during processes involving combustion

depends primarily on the efficiency of the combustion process itself. Highly efficient combustion results in essentially complete conversion of carbon and hydrogen to carbon dioxide and water. Inefficient burning in oxygen-poor atmospheres results in the formation of relatively high levels of PAHs. The amount of PAHs actually emitted to the atmosphere also depends on the efficiency of the pollution control equipment used.

The production of PAHs from man-induced and man-controlled combustion processes is by far the most significant and the easiest to quantify (Hangebrauck et al., 1967). In comparison, the quantities of PAHs formed by natural sources and processes are very small and difficult to estimate accurately. These sources provide the "natural background" concentrations for PAHs in the environment. It has been suggested that PAHs formed in natural combustion processes such as forest fires are structurally distinct from those produced in anthropogenic sources (Blumer et al., 1975).

To explain the presence of PAHs in fossil fuels in seemingly unpolluted soils and in marine sediments, it has been suggested that PAHs may also be formed biosynthetically by highly developed plants and microorganisms, plankton and algae, and by low temperature processes similar to those which bring about the transformation of plants and animals into peat and lignite (MOE, 1979, p. 45). However, while the possibility of PAH formation through such processes cannot be discounted, it remains largely unconfirmed and highly controversial. Thus the

biosynthetic formation of PAHs by plants, formerly thought to have been conclusively demonstrated, is now largely discredited by the negative results obtained with plants grown in absolutely unpolluted media.

The PAHs from the above-mentioned sources reach the soil and aquatic ecosystems by several routes, including dry fallout and precipitation (as both rain and snow), as well as washout and runoff. Industrial effluents, marine transportation and oil spills contribute PAHs directly to the aquatic environment. The contribution from a particular source will depend on many factors, including climate, geography, urbanization and industrialization. It has been suggested that PAHs are transported in air and water as adsorbed matter on particulates, especially particulates high in organic content (EPA, 1979).

PAHs have been found in living tissues and they have the potential to bioaccumulate. The calculated n-octanol/water coefficients were found to be good predictors of the bioaccumulation potential in Daphnia. It has been suggested that PAHs with four or less aromatic rings are rapidly metabolized and excreted from organisms and that therefore the bioaccumulation is only short-term (EPA, 1979).

In the environment, PAHs can degrade by several processes, such as photolysis, oxidation or metabolization in living matter (EPA, 1979). Probably the most important process, quantitatively, is photolysis or photooxidation, both in the atmosphere and in the aquatic environment.

Oxidation with ozone, chlorine dioxide or other chlorine compounds can also occur, especially in places such as water and wastewater treatment plants. On the other hand, uptake by aquatic organisms, followed by some biodegradation has also been reported. It has been suggested that bacteria can degrade PAHs much more completely than mammals can. The ease of degradation appears to be inversely related to the number of rings in the compound, with some compounds such as benzo (a) pyrene being almost totally resistant to transformation (EPA, 1979).

Under simulated environmental conditions, the ionic strength of water and the pH had no effect on benzo (a) pyrene degradation in aqueous solution or while adsorbed on calcium carbonate particles in an aqueous suspension (Suess, 1972; Andelman and Suess, 1971). Increased oxygen concentration, temperature, illumination and exposure time, however, increased the rate of degradation. This study led to the conclusion that the degradation of benzo (a) pyrene in natural waters will depend on the water depth, daily and seasonal fluctuations of solar radiation, ambient temperature and dissolved oxygen concentration. Consequently, the degradation rate constant will be higher in the upper layers of the water column, where illumination, temperature and oxygen concentrations are high, and will decrease with depth owing to reduced water clarity (resulting from suspended and colloidal matter, and biota), reduced illumination (resulting from the absorption of light by the water), and reduced temperature and oxygen concentration (Suess, 1972). It has been reported that the photolysis of benzo (a) pyrene in water containing

humic acids was five times slower than that in pure water. The photolysis was inhibited when the same compound was adsorbed on kaolinite clay. In deep, turbid, slow-moving rivers and lakes the importance of photolysis as a degradation process will be much less when compared with its importance in shallow, clear waters (EPA, 1979).

PAHs IN THE AQUATIC ENVIRONMENT

Polynuclear aromatic hydrocarbons enter the aquatic environment by a number of mechanisms, including precipitation and fallout from atmospheric aerosols, domestic and industrial wastewater discharges, runoff from city streets, asphalt-covered road surfaces, and oil spills. Levels of PAHs found in aquatic systems have been the subject of many reviews (Borneff, 1977; IARC, 1973). PAH levels have been reported to range from 1 to 100 ng/L in ground water, from 10 to 25 ng/L in treated river and lake waters, from 25 to 100 ng/L in surface waters, over 100 ng/L in contaminated surface waters, and around 100 000 ng/L in raw sewage (Borneff, 1977).

As mentioned, PAHs are adsorbed very readily onto suspended, especially organic, matter. Although probably slower than photolysis, especially in fast-moving rivers, sedimentation is an important process in the removal of PAHs. For example, a partition coefficient of 150 000 between sediment and water has been reported for benzo (a) pyrene, one of the compounds considered in the present study. In a simulated river, 83%

of the same compound was adsorbed onto suspended solids (EPA, 1979). Large amounts of PAHs were found adsorbed on organic and inorganic suspended or bottom sediments in rivers and lakes (Gump et al., 1977; Strosher and Hodgson, 1975). Synthetic detergents or natural surface-active agents such as humic and fulvic acids can solubilize PAHs.

Removal of PAHs in water treatment plants may be accomplished through mechanical means such as sedimentation, sand filtration and filtration on activated carbon, or by chemical processes such as ozonation or treatment with chlorine compounds, particularly chlorine dioxide (MOE, 1979).

Generally about two thirds of the suspended particles containing PAHs may be removed by the combination of sedimentation and sand filtration, but occasionally a removal efficiency of up to 90% may be observed, especially where PAHs are associated with large particles (Borneff, 1977). The coagulation of suspended particulate matter by the addition of chemical agents, such as $FeCl_3$, usually helps in improving removal efficiency. Filtration through activated carbon has been shown in laboratory tests to eliminate up to 99% of PAHs including those present in solution. However, in actual practice in water treatment plants, the efficiency is reduced to around 90%, owing to loss of activity of the filter material which results from prolonged use (Borneff, 1977).

RESULTS

The detailed analytical results from the present study are given in Appendix B. Appendix C summarizes these data by type of sampling site. Although at the time of sampling the various sampling sites were given a narrative description, no specific criteria for describing a site were included in the project design. Using the available descriptions, the sampling sites were grouped as follows:

		Station Locations (Appendix A)
A.	Fish processing/urban	1
	Fish plant/sewage	4
B.	Pulp, paper and food processing	8
	Pulp, paper/urban	2
C.	Urban	5, 13
D.	Industrial/urban	6, 29
E.	Industrial	3,10,11,12,14,18,20,21,22,23
F.	Coal mining/development	26
	Coal mining/urban	7
G.	Agriculture (fruit)/urban	27
H.	Pristine	9,15,16,17,19,24,25,28,30

The minimum, mean and maximum values were computed for each of the above groups and for each of the six PAHs measured in this study. These values are given in Appendix C.

DISCUSSION

The samples collected were from a broad and varied spectrum of environments, ranging from sites that could be considered as "remote" or pristine to sites in the close proximity of urban and industrial activities. The lack of guidelines in the selection of sampling sites from region to region resulted in large fluctuations in the number of results collected at various location types. The number of observations varied from as few as six (fish processing/urban, fish plant/sewage groups) to as many as 33 (pristine group). In addition, many results were either "trace" or "not detected." In certain cases (pristine, agricultural (fruit)/urban and industrial), most of the results fell into these categories. The lack of consistency in site location combined with the lack of information on the sample size, its organic content and the particle size distribution make any interpretation of the data very difficult.

The graph in Figure 3 provides a rough indication of the range of values for each parameter analyzed in each of the A-H location categories. It shows that the highest PAH concentrations in bottom sediments are found in the vicinity of fish and food processing, and pulp and paper industries. Urban environment also seems to contribute small amounts to the concentration of PAHs in sediments. As expected, in the "pristine" environments low concentrations were found except for benzo (b) fluoranthene, benzo (g,h,i) pyrene and indeno (1,2,3-cd) pyrene. The low concentrations in the coal mining areas and even agricultural land were unexpected. These results warrant further investigation, particularly in light of the lack of particle size data.

FIGURE 3. MINIMUM, MEAN AND MAXIMUM VALUES FOR SIX PAHs IN BOTTOM SEDIMENTS GROUPED BY TYPE OF SAMPLING SITE

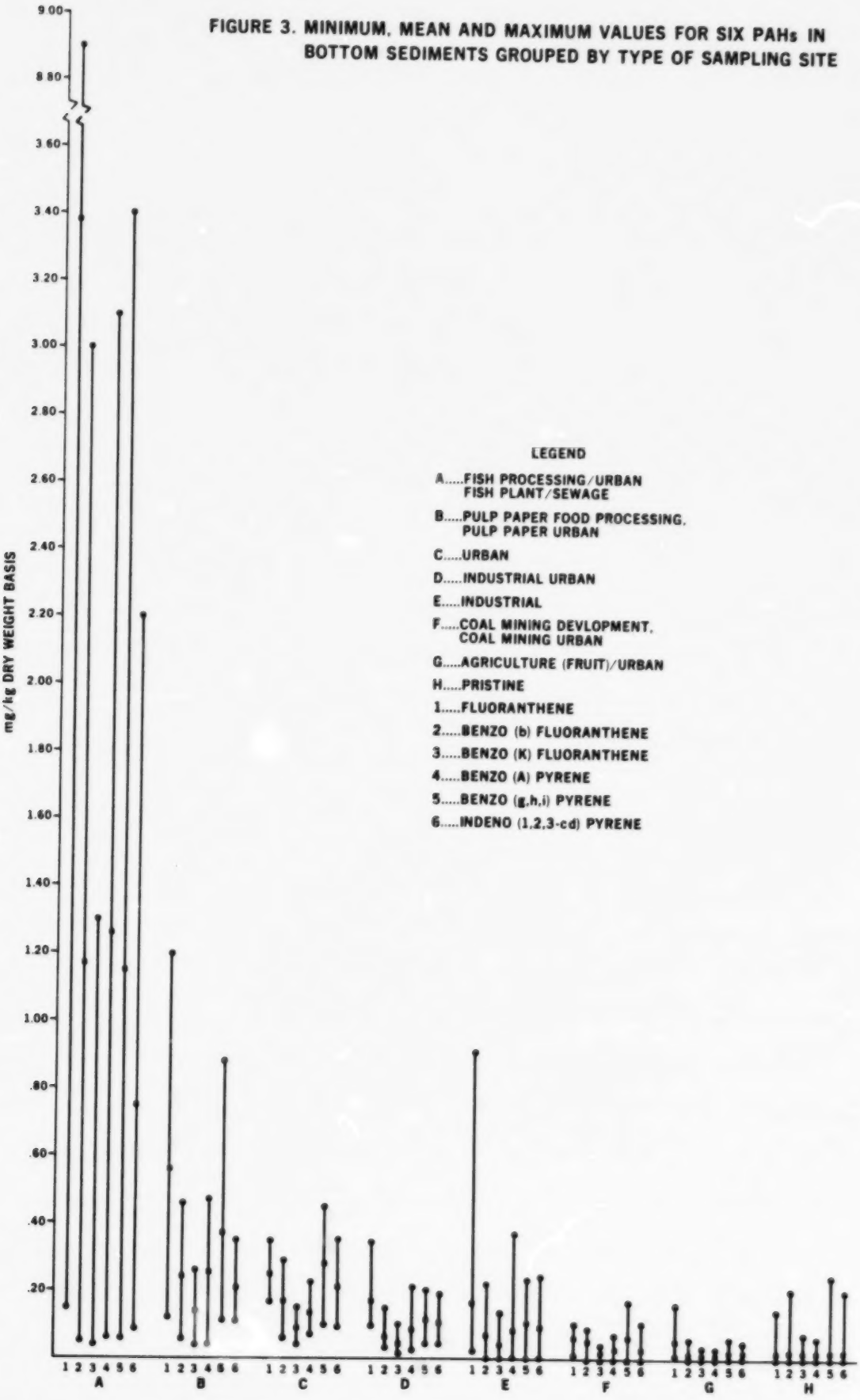


Table 4. Concentration of PAHs in Water and Sediment Samples from St. John's Harbour (Nfld)

	Water (mg/L)	Sediment (mg/kg) dry wt average*	Range
Fluoranthene	0.005	0.17	0.10-0.21
Benzo (b) fluoranthene	0.003	0.06	0.03-0.10
Benzo (k) fluoranthene	0.002	0.04	Trace. -0.06
Benzo (a) pyrene	0.003	0.07	0.03-0.10
Benzo (g,h,i) pyrene	0.006	0.11	0.07-0.14
Indeno (1,2,3-cd) pyrene	0.005	0.11	0.04-0.17

*Average of three samples

These results show once again how important it is to standardize quality assurance protocols prior to undertaking a study of this type. Aspects such as site selection, number of samples to be collected, particle size analysis, organic content analysis, and efficient quality control/quality assurance programs must be considered, beginning in the planning phase of such a study.

Recently, Water Quality Branch, Atlantic Region (WQB-AR, 1984 a, b) has published the results of two surveys for toxic chemicals, including PAHs, in water and sediments (Table 4). Among the locations sampled some were the same as the present study, and the concentrations found were, in general, higher by a factor of three to four. It must be noted that the analytical method used in this study was different from the one used in the WQB-AR studies.

Results for the two Lake St. Francis locations (sites 10 and 11) were similar to results obtained in another study (Novalab Ltd., 1982).

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APPENDIX A

Detailed Station Locations

1. St. John's Harbour, 400 m N of MOT Coast Guard Terminal (53NF02ZM0002), Newfoundland.
2. Humber Arm at Church Cove, 100 m NW of Gulf Oil Pier, Humber West (53NF02YK0001), Newfoundland.
3. Sydney Harbour, 200 m SE of Sydney Engineering and Drydock (53NS01JI0001), Nova Scotia.
4. Liverpool Bay, 150 m W of Mersey Bowater Pulp Mill Wharf (53NS01ED0002), Nova Scotia.
5. Summerside Harbour 100 m S 25°W from southwestern corner of Queens Wharf (53PEI01CB0006), Prince Edward Island.
6. Saint John Harbour, 50 m N of Pier 9 (52NB01AP0012), New Brunswick.
7. Grand Lake, about 700 m from Jemseg River at black channel marker (51NB01AØ0019), New Brunswick.
8. Saint John River at Grand Falls, 450 m above dam, Victoria County (51NB01AF0006), New Brunswick.
9. Lac de l'Est, Compté Kamouraska, Quebec.
10. Eastern part of Lake St. Francis, Quebec.
11. Western part of Lake St. Francis, Quebec.
12. St. Lawrence River downstream from Cornwall, Ontario.
13. Lake Ontario near Kingston, Ontario.
14. Upper Niagara River, Ontario.

15. Moose River near mouth, Ontario.

16. Goulais River downstream of Highway 17 (three locations, T_1, T_2, T_3 along one transect), Ontario.

17. Severn River near mouth, Ontario.

18. Red River at Selkirk, Manitoba.

19. Lake Minnewasta on Highway 434, Manitoba.

20. Qu'Appelle River Delta, Pasqua Lake, Saskatchewan.

21. Boundary Reservoir, Long Creek, Saskatchewan.

22. North Saskatchewan River Delta, Tobin Lake, Saskatchewan.

23. South Saskatchewan River Delta, Lake Diefenbaker, Saskatchewan.

24. Athabaska River at Jackfish Creek, Alberta.

25. Bow Lake, Banff National Park, Alberta.

26. Elk River at Hosmer (two stations S_1, S_2), British Columbia.

27. Okanagan River near Oliver (two stations S_1, S_2), British Columbia.

28. North Thompson River near Blue River, British Columbia.

29. Fraser River, North arm above Oak Street Bridge (two stations S_1, S_2), British Columbia.

30. Stikine River above Canyon, British Columbia.

APPENDIX B

Detailed Analytical Results

The results of the 105 environmental sediment samples, corrected for recovery, are expressed in milligrams per kilogram on a dry weight basis. Entries of TRACE and ND are defined as follows:

TRACE — Indicates that the compound was detected but at a level below the limits of quantitation. The limit of quantitation was approximated to be 0.01 mg/kg, uncorrected for recovery.

ND — Indicates that the compound was not detected. The limit of detection was approximated to be in the range of 0.001-0.005 mg/kg.

Abbreviations

Fluoranthene:	FL
Benzo (b) fluoranthene:	B(b)F
Benzo (k) fluoranthene:	B(k)f
Benzo (a) pyrene:	B(a)P
Benzo (g,h,i) pyrene:	B(ghi)P
Indeno (1,2,3-cd) pyrene:	IP

Reference: Cantest Ltd. 1982. Environmental Monitoring of Polynuclear Aromatic Hydrocarbons. Analysis of Sediment Samples. DSS File No. 5055KE 145-1-0451, Vancouver, British Columbia.

Table B-1. Detailed Analytical Results

Location	Sample No.	Concentration (mg/kg - dry weight basis) FL	B(b)F	B(k)F	B(a)P	B(ghi)P	IP
1	5	8.9	3.0	1.3	3.1	3.4	2.2
	32	4.9	2.0	0.90	2.1	1.5	1.0
	59	5.8	1.8	0.77	2.1	1.7	1.0
2	4	1.2	0.46	0.22	0.47	0.52	0.35
	31	0.58	0.33	0.21	0.34	0.88	0.21
	58	1.1	0.44	0.26	0.44	0.42	0.33
3	7	12.0	11.0	4.20	13.0	7.0	9.6
	34	21.0	11.0	4.90	13.0	9.7	7.1
	61	12.0	14.0	6.10	15.0	9.7	7.5
4	6	0.20	0.05	0.07	0.08	0.10	0.10
	33	0.15	0.06	0.04	0.06	0.06	0.09
	60	0.32	0.10	0.06	0.09	0.15	0.11
5	8	0.23	0.06	0.04	0.10	0.10	0.09
	35	0.17	0.06	0.04	0.07	0.15	0.10
	62	0.35	0.22	0.07	0.08	0.17	0.10
6	3	0.21	0.04	0.06	0.08	0.11	0.17
	30	0.19	0.10	0.06	0.10	0.14	0.11
	57	0.10	0.03	Trace	0.03	0.07	0.04
7	2	0.08	ND	ND	ND	ND	ND
	29	Trace	ND	ND	ND	ND	ND
	56	0.07	0.03	0.02	0.02	0.09	0.04
8	1	0.19	0.06	0.04	0.10	0.16	0.13
	28	0.12	0.09	0.05	0.04	0.11	0.11
	55	0.17	0.08	0.06	0.08	0.14	0.13
9	11	0.10	0.13	0.05	0.03	0.24	0.14
	38	0.13	0.20	0.07	0.04	0.22	0.20
	65	0.14	0.15	0.06	0.06	0.18	0.18
10	10	0.14	0.12	0.07	0.10	0.20	0.15
	37	0.19	0.07	0.06	0.11	0.17	0.16
	64	0.10	0.11	0.05	0.08	0.15	0.10
11	9	0.14	0.12	0.05	0.09	0.15	0.13
	36	0.11	0.12	0.07	0.08	0.17	0.16
	63	0.12	0.13	0.06	0.10	0.17	0.14

ND - Not detected.

Table B-1. Continued

Location	Sample No.	Concentration (mg/kg - dry weight basis) FL	B(b)F	B(k)F	B(a)P	B(ghi)P	IP
12	18	0.19	0.03	0.11	0.13	0.15	0.20
	45	0.30	0.21	0.11	0.19	0.22	0.19
	72	0.23	0.16	0.09	0.13	0.19	0.18
13	15	0.19	0.12	0.09	0.12	0.45	0.33
	42	0.21	0.25	0.14	0.19	0.38	0.31
	69	0.32	0.29	0.15	0.22	0.42	0.35
14	17	0.08	0.03	0.03	0.04	0.15	0.11
	44	0.14	0.09	0.05	0.07	0.13	0.10
	71	0.24	0.11	0.06	0.11	0.18	0.15
15	16	Trace	ND	ND	ND	ND	ND
	43	0.02	Trace	Trace	Trace	0.05	Trace
	70	Trace	Trace	ND	ND	ND	ND
$16T_1$	12	ND	ND	ND	ND	ND	ND
	39	Trace	ND	ND	ND	ND	ND
	66	Trace	ND	ND	ND	ND	ND
$16T_2$	13	ND	ND	ND	ND	ND	ND
	40	Trace	ND	ND	ND	ND	ND
	67	Trace	ND	ND	ND	ND	ND
$16T_3$	14	Trace	ND	ND	ND	ND	ND
	41	0.03	Trace	Trace	Trace	Trace	Trace
	68	0.05	Trace	Trace	Trace	Trace	Trace
17	19	ND	ND	ND	ND	ND	ND
	46	Trace	ND	ND	ND	ND	ND
	73	Trace	Trace	ND	ND	ND	ND
18	82	0.81	0.22	0.13	0.33	0.23	0.24
	83	0.91	0.15	0.05	0.37	0.21	0.21
	84	0.28	0.11	0.07	0.16	0.11	0.17
19	85	0.04	Trace	ND	ND	ND	ND
	86	0.03	Trace	ND	ND	ND	ND
	87	0.02	Trace	ND	ND	ND	ND
20	88	0.02	ND	ND	ND	ND	ND
	89	0.02	ND	ND	ND	ND	ND
	90	0.03	ND	ND	ND	ND	ND
21	97	0.03	ND	ND	ND	ND	ND
	98	0.04	ND	ND	ND	ND	ND
	99	0.04	ND	ND	ND	ND	ND

Table B-1. Concluded

Location	Sample No.	Concentration (mg/kg-dry weight basis)					
		FL	B(b)F	B(k)F	B(a)P	B(ghi)P	IP
22	91	0.06	ND	ND	ND	ND	ND
	92	0.05	ND	ND	ND	ND	ND
	93	0.07	ND	ND	ND	ND	ND
23	94	0.02	ND	ND	ND	ND	ND
	95	0.02	ND	ND	ND	ND	ND
	96	0.04	ND	ND	ND	ND	ND
24	103	0.02	ND	ND	ND	ND	ND
	104	Trace	ND	ND	ND	ND	ND
	105	Trace	ND	ND	ND	ND	ND
25	100	Trace	ND	ND	ND	ND	ND
	101	Trace	ND	ND	ND	ND	ND
	102	Trace	ND	ND	ND	ND	ND
$26S_1$	22	0.05	0.03	Trace	Trace	0.10	ND
	49	0.07	0.08	0.03	0.04	0.14	0.07
	76	0.09	0.07	0.03	0.06	ND	ND
$26S_2$	23	0.03	0.03	Trace	Trace	ND	ND
	50	0.06	0.09	0.03	0.07	0.17	0.11
	77	0.10	0.09	0.04	0.06	0.07	0.06
$27S_1$	24	0.04	Trace	ND	Trace	ND	ND
	51	0.04	Trace	Trace	0.03	0.04	Trace
	78	0.02	ND	ND	ND	ND	ND
$27S_2$	25	0.16	0.06	0.03	0.03	0.06	0.05
	52	Trace	ND	ND	ND	ND	ND
	79	0.02	ND	ND	ND	ND	ND
28	21	Trace	ND	ND	ND	ND	ND
	48	ND	ND	ND	ND	ND	ND
	75	Trace	Trace	ND	ND	ND	ND
$29S_1$	26	0.13	0.05	0.03	0.04	0.09	0.05
	53	0.11	0.06	0.02	0.02	0.08	0.04
	80	0.14	0.04	0.03	0.06	0.04	0.08
$29S_2$	27	0.18	0.09	0.07	0.11	0.14	0.12
	54	0.11	0.04	0.02	0.03	0.09	0.08
	81	0.35	0.15	0.10	0.21	0.20	0.19
30	20	ND	ND	ND	ND	ND	ND
	47	Trace	Trace	ND	ND	ND	ND
	74	Trace	Trace	ND	ND	ND	ND

APPENDIX C

Summary Statistics for PAH Concentration in Bottom Sediment Samples by Type of Sampling Site

For the purpose of this appendix, trace values will be identified by (T), and ND will represent non-detectable values. As in Appendix B, values of 0.01 (mg/kg) and 0.001 (mg/kg), respectively, represent trace and non-detectable..

Abbreviations

Fluoranthene:	FL
Benzo (b) fluoranthene:	B(b)F
Benzo (k) fluoranthene:	B(k)F
Benzo (a) pyrene:	B(a)P
Benzo (g,h,i) pyrene:	B(g,h,i)P
Indeno (1,2,3-cd) pyrene:	IP

Table C-1. Group A: Fish Processing/Urban, Fish Plant/Sewage

	FL	B(b)F	B(k)F	B(a)P	B(ghi)P	IP
		Concentration (mg/kg - dry weight basis)				
Mean	3.38	1.17	0.52	1.26	1.15	0.75
Median	2.61	0.95	0.42	1.10	0.83	0.56
Standard deviation	3.70	1.27	0.54	1.34	1.33	0.84
Minimum	0.15	0.05	0.04	0.06	0.06	0.09
Maximum	8.9	3.0	1.3	3.1	3.4	2.2
Number of samples	6	6	6	6	6	6

Table C-2. Group B: Pulp, Paper and Food Processing, Pulp, Paper/Urban

	FL	B(b)F	B(k)F	B(a)P	B(ghi)P	IP
		Concentration (mg/kg - dry weight basis)				
Mean	0.56	0.24	0.14	0.25	0.37	0.21
Median	0.39	0.21	0.14	0.22	0.29	0.17
Standard deviation	0.49	0.19	0.10	0.19	0.30	0.11
Minimum	0.12	0.06	0.04	0.04	0.11	0.11
Maximum	1.2	0.46	0.26	0.47	0.88	0.35
Number of samples	6	6	6	6	6	6

Table C-3. Group C: Urban

	FL	B(b)F	B(k)F	B(a)P	B(ghi)P	IP
	Concentration (mg/kg - dry weight basis)					
Mean	0.25	0.17	0.09	0.13	0.28	0.21
Median	0.22	0.17	0.08	0.11	0.28	0.21
Standard deviation	0.07	0.10	0.05	0.06	0.15	0.13
Minimum	0.17	0.06	0.04	0.07	0.10	0.09
Maximum	0.35	0.29	0.15	0.22	0.45	0.35
Number of samples	6	6	6	6	6	6

Table C-4. Group D: Industrial/Urban

	FL	B(b)F	B(k)F	B(a)P	B(ghi)P	IP
	Concentration (mg/kg - dry weight basis)					
Mean	0.17	0.06	0.04	0.08	0.11	0.10
Median	0.14	0.05	0.03	0.06	0.09	0.08
Standard deviation	0.08	0.04	0.03	0.06	0.05	0.06
Minimum	0.10	0.03	0.01(T)	0.02	0.04	0.04
Maximum	0.35	0.15	0.10	0.21	0.20	0.19
Number of samples	9	9	9	9	9	9

Table C-5. Group E: Industrial

	FL	(Bb)F	B(k)F	B(a)P	B(ghi)P	IP
	Concentration (mg/kg - dry weight basis)					
Mean	0.16	0.07	0.04	0.08	0.10	0.09
Median	0.10	0.03	0.05	0.07	0.13	0.10
Standard deviation	0.22	0.07	0.04	0.10	0.09	0.09
Minimum	0.02	0.001(ND)	0.001(ND)	0.001(ND)	0.001(ND)	0.001(ND)
Maximum	0.91	0.22	0.13	0.37	0.23	0.24
Number of samples	27	27	27	27	27	27

Table C-6. Group F: Coal Mining , Coal Mining/Urban

	FL	B(b)F	B(k)F	B(a)P	B(ghi)P	IP
	Concentration (mg/kg - dry weight basis)					
Mean	0.06	0.05	0.02	0.03	0.06	0.03
Median	0.07	0.03	0.02	0.02	0.07	0.001(ND)
Standard deviation	0.03	0.04	0.01	0.03	0.07	0.04
Minimum	0.01(T)	0.001(ND)	0.001(ND)	0.001(ND)	0.001(ND)	0.001(ND)
Maximum	0.10	0.09	0.04	0.07	0.17	0.11
Number of samples	9	9	9	9	9	9

Table C-7. Group G: Agriculture (Fruit)/Urban

	FL	B(b)F	B(k)F	B(a)P	B(ghi)P	IP
	Concentration (mg/kg - dry weight basis)					
Mean	0.05	0.01	0.01	0.01	0.02	0.01
Median	0.02	0.006(T)	0.001(ND)	0.006(T)	0.001(ND)	0.001(ND)
Standard deviation	0.06	0.02	0.01	0.01	0.03	0.02
Minimum	0.01(T)	0.001(ND)	0.001(ND)	0.001(ND)	0.001(ND)	0.001(ND)
Maximum	0.16	0.06	0.03	0.03	0.06	0.05
Number of samples	6	6	6	6	6	6

Table C-8. Group H: Pristine

	FL	B(b)F	B(k)F	B(a)P	B(ghi)P	IP
	Concentration (mg/kg - dry weight basis)					
Mean	0.02	0.02	0.01	0.01	0.02	0.02
Median	0.01(T)	0.001(ND)	0.001(ND)	0.001(ND)	0.001(ND)	0.001(ND)
Standard deviation	0.03	0.05	0.02	0.01	0.06	0.05
Minimum	0.001(ND)	0.001(ND)	0.001(ND)	0.001(ND)	0.001(ND)	0.001(ND)
Maximum	0.14	0.20	0.07	0.06	0.24	0.20
Number of samples	33	33	33	33	33	33

APPENDIX D. Correction Factors for PAH Recovery Losses

DRY WEIGHT CONCENTRATION RANGE	<0.04	0.04-0.08	0.08-0.12	0.12-0.16	0.16-0.20	0.20-0.32	>0.32
FLUORANTHENE	1.83	1.39	1.19	1.10	1.06	1.00	1.00
BENZO (b) FLUORANTHENE	1.77	1.50	1.33	1.22	1.14	1.08	1.00
BENZO (k) FLUORANTHENE	1.77	1.50	1.33	1.22	1.14	1.08	1.00
BENZO (a) PYRENE	1.77	1.50	1.33	1.22	1.14	1.08	1.00
BENZO (g,h,1) PERYLENE	2.94	2.13	1.71	1.37	1.19	1.10	1.00
INDENO (1,2,3-cd) PYRENE	2.94	2.13	1.71	1.37	1.19	1.10	1.00

NOTE: All results expressed as milligrams per kilogram dry weight basis.